ARTICLE IN PRESS

Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Original Article

Role of boron addition on phase composition, microstructural evolution and mechanical properties of nanocrystalline SiBCN monoliths

Daxin Li[b], Zhihua Yang[a,b,*], Dechang Jia[a,b,*], Xiaoming Duan[a,b], Yu Zhou[b], Dongli Yu[c], Yongjun Tian[c], Zihuan Wang[d], Yinglong Liu[d]

[a] State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Heilong Jiang, Harbin 150001, China
[b] Institute for Advanced Ceramics, School of Materials Science and Engineering, Harbin Institute of Technology, Heilong Jiang, Harbin 150080, China
[c] State Key Laboratory of Metastable Materials Science and Technology, Yanshan University, Qinhuangdao 066004, China
[d] Beijing Institute of Control Engineering, Beijing 100094, China

ARTICLE INFO

Keywords:
SiBCN
BN(C)
Microstructural evolution
Mechanical alloying
Mechanical properties

ABSTRACT

Nanocrystalline SiBCN monoliths with the same Si/C/N mole ratio and various boron additions ranged from 0 to 3.0 mol were prepared by mechanical alloying plus reactive hot pressing methods. Correction of boron content and microstructural/morphological evolution was investigated in detail by XRD, SEM, TEM and STEM-EDX structure characterization. Except for SiC and BN(C), boron addition contributes to B_xC formation. Besides, boron addition promotes the crystallization of SiC, leading to the formation of poor crystallinity of spherical structures in inner SiC. Furthermore, boron addition significantly promotes the grain growth of SiC and B_xC and therefore increases the relative volume ratios of B_xC/BN(C) and B_xC/SiC. Amorphous-like BN(C) changes to belt-like structures as boron addition increases. The new formed B_xC effectively contributes to the improvement of Vicker's hardness while pull-out of BN(C) belt-like structures benefits the fracture toughness.

1. Introduction

In the past decades, strong and thermodynamically stable materials have been investigated widely as such materials are considered as potential candidates for use in high-temperature structural and multi-functional heat-resistant components at extreme environments [1–3]. SiBCN-based materials have attracted extensively scientific and engineering interest due to their excellent thermal stability, desirable high-temperature creep/oxidation resistance and good mechanical properties [4–6]. The remarkable high-temperature stability of the amorphous nature up to ~2200 °C is the main structure feature for SiBCN-based materials [7]. The unique properties of SiBCN-based materials result from their unusual strictures.

The current efforts of SiBCN-based materials mainly focused on the synthesis of multiple polymer precursors to evaluate the chemical composition on the thermal stability [7–9]. Another research focus was aimed at understanding the microstructural evolution during heat-treatment including the polymer to ceramic transition, phase separation and demixing of amorphous nanodomains and crystallization behavior [9–11]. Generally, SiBCN-type materials below a certain temperature (~1300 °C) were X-ray amorphous, but wide-angle neutron- and X-ray scattering as well as nuclear magnetic resonance investigations brought insight on atomic short-range ordering in structural units of the SiC_iN_{4-i} (i = 1–4) tetrahedral and separated B-N-C nanodomains [12–14]. Further annealing at higher temperatures led to initiate nucleation, growth and coarsening forming nano-materials [14]. XRD investigations revealed a two-stage crystallization process including initial formation of nano-SiC followed by nano-Si_3N_4 in a second stage [15]. The crystallization of amorphous structures strongly impacted the attendant physical and mechanical properties of these materials. For example, Kumar et al. reported that nano-SiBCN composed of nano-SiC and $-Si_3N_4$ crystals presented a better creep resistance than the amorphous ones [16].

A number of attempts have been made to illustrate the crystallization behavior of SiBCN-based materials [17–19]. It was reported that boron is essential for the crystallization process [19]. The transformation of amorphous structure into nanocrystals depended on the overall ceramic composition, especially the amount of boron [20]. For example, a strong hindering effect of boron on Si_3N_4 degradation was reported [21–23]. The sizes of micro-Si_3N_4 changed to a nanoscale with the increases of boron content. Moreover, the ratio of α-Si_3N_4/β-Si_3N_4 in nanocrystalline matrix decreased as boron content increased. However, further experimental study showed that the controlling mechanisms of Si_3N_4 crystallization including continuous nucleation and

---

* Corresponding authors at: State Key Laboratory of Advanced Welding and Joining, Harbin Institute of Technology, Heilong Jiang, Harbin 150001, China.
E-mail addresses: zhyang@hit.edu.cn (Z. Yang), dcjia@hit.edu.cn (D. Jia).

https://doi.org/10.1016/j.jeurceramsoc.2017.11.054
Received 15 August 2017; Received in revised form 20 November 2017; Accepted 25 November 2017

Please cite this article as: Li, D., Journal of the European Ceramic Society (2017), https://doi.org/10.1016/j.jeurceramsoc.2017.11.054

diffusion-controlled growth are boron content-independent [24]. By contrast, the boron should be at least partially responsible for the nucleation of Si_3N_4. Using the improving thermodynamic model confirmed the effects of boron content on driving force for crystallization, especially contributed to SiC crystallization [22]. The crystallization of SiC can proceed by a very rapid pathway [25].

Recently, mechanical alloying plus reactive sintering techniques were adopted to prepare dense SiBCN monoliths [26–33]. The constituent element ratios designed by mechanical alloyed cubic silicon, boron, hexagonal boron nitride and graphite in a selected mole ratio gives a chance to optimize the final phase composition and microstructures of as-sintered monoliths [26–30]. In a previous study, hot-pressed $Si_2B_1C_3N_1$ monoliths crystallized to form β-SiC, BN(C) and α-SiC at 1500 °C, 1600 °C and 1700 °C, respectively [26]. It thus suggested that the crystallization depended significantly on the sintering temperature. The crystallization behavior of highly dense amorphous $Si_2B_1C_3N_1$ monoliths prepared by high-pressure-low-temperature-sintering was also discussed [27]. Highly dense amorphous monoliths retained their amorphous nature accompanied with partial phase segregation at 1100–1200 °C, followed by initiation of nucleation at 1200–1250 °C, and then growth and coarsening of SiC and BN(C) at elevated temperatures. In another work, the phase composition and microstructural evolution of carbon-lean to –rich hot-pressed SiBCN monoliths were investigated [28]. Results showed that the phase composition and microstructural/morphological evolution were carbon content-dependent. SiBCN monoliths containing 2–3 mol carbon with tailor-made microstructures offered satisfying mechanical properties, therefore can meet the practical applications.

Despite many reports concerning the phase transformation and crystallization of amorphous SiBCN-type materials, the role of boron on microstructural evolution and mechanical properties of nanocrystalline SiBCN monoliths was rarely reported. Herein, in a first attempt, a systematic study was undertaken to evaluate the phase composition and microstructural evolution of the nanocrystalline monoliths. Meanwhile, the effects of boron addition on chemical bonds and mechanical properties were also investigated. A second series of attempts, we began by discussing the promoting role of boron on SiC crystallization, boron content-dependent BN(C) morphological evolution, and relationship between microstructures and mechanical properties.

2. Experimental procedures

2.1. Materials preparation

Amorphous SiBCN powders were produced starting from commercial raw materials [32]:

a. Cubic Silicon (99.9% in purity, 75.0 μm, Beijing Mountain Technical Development Center, Beijing, China);
b. Graphite (99.5% in purity, 8.7 μm, Qingdao Huatai Lubricant Sealing S&T Co., Ltd., Qingdao, China);
c. Hexagonal BN (99.9% in purity, 0.6 μm, Advanced Technology & Materials Co., Ltd., Beijing, China);
d. Boron powders (99.9% in purity, 15 μm, Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China).

The chemical composition was designed as Si: B: C: N = 2: X: 2: 1 in a mole ratio. X represents the amount of boron content. Initially, the powder mixtures of ~17 g were sealed under Ar atmosphere in Si_3N_4 vials with 340 g Si_3N_4 balls, 10 mm in diameter. Thereafter, the powder mixtures were ball milled in a planetary miller (P4 Fritsch GmbH, Germany) with the rotation speed of the main disk set at 350 rpm and vials 600 rpm in reverse. The total milling time was 48 h and the machine was stopped for 10 min in every 50 min. After ball milling, the as-synthesized amorphous powders were grinded and sieved by a 20 mesh sieve. The powder mixtures mixed, milled, transported and stored were operated in Ar atmosphere.

Table 1
Composition design and sintering parameters of SiBCN monoliths with various boron additions.

Sample Codes	Composition	Mole ratio				Sintering parameters
		Si	C	BN	B	
0B	$Si_2B_1C_2N_1$	2	2.0	1	0	1900 °C/60 MPa/30 min/ 1 bar N_2
01B	$Si_2B_{1.1}C_2N_1$	2	2.0	1	0.1	
05B	$Si_2B_{1.5}C_2N_1$	2	2.0	1	0.5	
10B	$Si_2B_2C_2N_1$	2	2.0	1	1.0	
15B	$Si_2B_{2.5}C_2N_1$	2	2.0	1	1.5	
20B	$Si_2B_3C_2N_1$	2	2.0	1	2.0	
25B	$Si_2B_{3.5}C_2N_1$	2	2.0	1	2.5	
30B	$Si_2B_4C_2N_1$	2	2.0	1	3.0	

As-synthesized powders were loaded into a graphite die with diameter of 36 mm coated with BN. Subsequently the graphite die was sintered in 1 bar N2 by a hot-pressing system (Highmulti-10000 HP, Japan). The target temperature was kept at 1900 °C with a soaking time of 30 min. The uniaxial pressure of 60 MPa was used in parallel. The surface temperature of samples was monitored by an optical pyrometer in a range of 1200–2200 °C. Afterward, the graphite die was furnace cooled to room temperature. The as-sintered monoliths were grinded with SiC pastes (3000 mesh) to a surface roughness of 0.5 μm prior to testing. Table 1 provides the elemental composition design and sintering parameters of the investigated materials.

2.2. Microstructural and mechanical characterization

As for the mechanical properties, the as-sintered monoliths were polished and then cut into bars 30 × 3 × 4 mm and 20 × 2 × 4 mm (length by width by thickness), respectively. Just for the sake of accuracy, three-point bending test was adopted to determine the flexural strength and Young's modulus with a crosshead speed of 0.5 mm/min (20 mm outer space, on bars 30 × 3 × 4 mm). The configuration used in this test exposed the maximum area under a constant maximum stress. Fracture toughness, K_{Ic}, was evaluated by using single edge notched beam (SENB) method in flexure with a crosshead speed of 0.05 mm/min (16 mm outer space, on bars 20 × 2 × 4 mm). For each sample, at least three bars were tested to ensure a statistical distribution. Vicker's hardness, H_v, was measured with a load of 10 kg applied for 10 s using a tester (HVS-5, Laizhou, Huayin, Testing Instrument Corp., USA). Fifteen readings were recorded for each sample and an average value was reported here.

The phase composition of the as-sintered SiBCN monoliths was determined by X-ray diffractometer (40 kV/100 mA, Cu-K_α, Rigaku Corp., Japan) with a scanning speed of 4°/min and angles ranged from 10 to 90°. The fractural morphologies of the as-sintered monoliths were acquired by using a scanning electron microscope (SEM, 20 kV, HELIO Nanolab 600i, USA). The microstructures were characterized by using an FEI Tecnai G^2 F30 microscope operated at 200 kV. Scanning transmission electron microscopy (STEM, Talos F200x, 200 kV) and energy dispersive X-ray (EDX, INCA Energy 300, Oxford Instruments, UK) analyses were employed by using high angle annular dark field (HAADF), high resolution TEM (HRTEM), selected-area electron diffraction (SAED) and inverse fast Fourier transformation (IFFT) techniques. X-ray photoelectron spectrometer (XPS, PHI 5000 Versaprobe II) and Raman spectroscopy (Ventana-532-RAMAN, 532 nm nano-laser excitation, Ocean Optics Asia) were adopted to study the chemical bonding states of B with an Al-K_α energy source. The signal curves were fitted by peak addition method using Gaussian-Lorentzian peak approximations and Shirley background reduction.